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## Nitrogen Adsorption and Hydrogenation on a $\text{MoFe}_6\text{S}_9$ Complex

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The enzyme nitrogenase catalyzes the biological nitrogen fixation where  $\text{N}_2$  is reduced to  $\text{NH}_3$ . Density functional calculations are presented of the bonding and hydrogenation of  $\text{N}_2$  on a  $\text{MoFe}_6\text{S}_9$  complex constructed to model aspects of the active site of nitrogenase.  $\text{N}_2$  is found to bind end on to one of the Fe atoms. A complete energy diagram for the addition of hydrogen to the  $\text{MoFe}_6\text{S}_9$  complex with and without  $\text{N}_2$  is given, and a mechanism for ammonia synthesis is proposed on this basis. [S0031-9007(99)09178-4]

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The enzyme nitrogenase catalyzes the biological nitrogen fixation, where ammonia is synthesized by the reaction  $\text{N}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow 2\text{NH}_3 + \text{H}_2$ . Nitrogenase consists of the Fe protein and the MoFe protein. During association of the two proteins, electrons are transferred from the Fe protein to the active site in the MoFe protein along with hydrolysis of adenosine triphosphate (ATP) [1]. The active site, where  $\text{N}_2$  binds and reacts, is believed to be a metal-sulfide cluster ( $\text{MoFe}_7\text{S}_9$ ) named the FeMo cofactor (FeMoco). The geometrical structure of the FeMoco [2,3] has been established recently, and a considerable amount of insight has been obtained about the overall kinetics of the hydrogenation process [4]. The binding site of  $\text{N}_2$  and the atomistic mechanism of  $\text{N}_2$  hydrogenation to ammonia are, however, still largely unknown. In the present Letter, we use density functional calculations to gain further insight into the interaction of nitrogen and hydrogen with the FeMoco. We study the adsorption and hydrogenation of  $\text{N}_2$  on a  $\text{MoFe}_6\text{S}_9$  complex chosen to model parts of the FeMoco. We establish the preferred binding site for  $\text{N}_2$  interacting with the Fe part of the complex, and show how the addition of hydrogen atoms (or electrons and protons) to the complex can lead to a gradual reduction of  $\text{N}_2$  to  $\text{NH}_3$ . We also investigate the simultaneous formation of  $\text{H}_2$ .

Because of the complexity of the FeMoco, theoretical insight into its bonding to  $\text{N}_2$  has mainly been through rather simple, but physically transparent model calculations of the electronic structure [5]. Recently, density functional theory (DFT) with a nonlocal description of exchange and correlation effects [6] has provided new hope for a reasonably accurate description of elementary chemical processes in complex systems. The first density functional calculations describing the bonding of  $\text{N}_2$  to the FeMoco were due to Dance [7]. He considered  $\text{N}_2$  adsorption on a quite complete model of the FeMoco but did not consider hydrogenation in detail. Most recently Siegbahn *et al.* [8] have used a hybrid DFT method to study  $\text{N}_2$  bonding on a series of Fe-S compounds. They have also looked at hydrogenation of  $\text{N}_2$ , however, only for  $\text{N}_2$  binding to a Fe dimer model.

In the present Letter we go one step further and consider a large FeMoco model and the complete hydrogenation of  $\text{N}_2$  in detail. Our study is based on fully self-consistent density functional calculations performed by expanding the wave functions in plane waves and describing the ion cores by nonlocal soft (S) and Vanderbilt ultrasoft (H, N, Fe, and Mo) pseudopotentials [9]. Plane waves with kinetic energies up to 25 Ry are used. Exchange and correlation effects are described within the generalized gradient approximation of Ref. [6]. The self-consistent electron density is determined by iterative diagonalization of the Kohn-Sham Hamiltonian, Fermi population of the Kohn-Sham states ( $k_B T = 0.1$  eV), and Pulay mixing of the resulting electronic density. All total energies have been extrapolated to  $k_B T = 0$  eV. Complete structural relaxation is made for each configuration studied. The same approach has proven able to describe in detail  $\text{N}_2$  activation on Ru and Fe surfaces [10].

To include all the atoms of the FeMoco and its ligands (Fig. 1) in the DFT calculations requires a huge unit cell and is therefore computationally extremely demanding. This is, in particular, true when studying not only the structure, but also chemical reactions on the cluster. To make the problem tractable, we have constructed a simple model compound (Fig. 1) by removing the end Fe atom and continuing the cluster periodically. In this way we decrease the size of the problem considerably, and at the same time all the other Fe, Mo, and S atoms have the correct coordination number. The compound is periodic in one direction ( $c$  axis), and in the calculations we repeat the structure periodically in the other two directions ( $a$  axes). The resulting unit cell is hexagonal with side lengths  $a = 9.5$  Å and  $c = 7.75$  Å. The value of  $c$  is chosen to minimize the total energy of the system. The first Brillouin zone is sampled with two equally spaced  $k$ -points along the  $c^*$  axis.

We have checked that the lowest energy structure of the model compound is very similar to the one determined experimentally for the FeMoco (Fig. 1, Table I). The ground state of our model system is found to have a

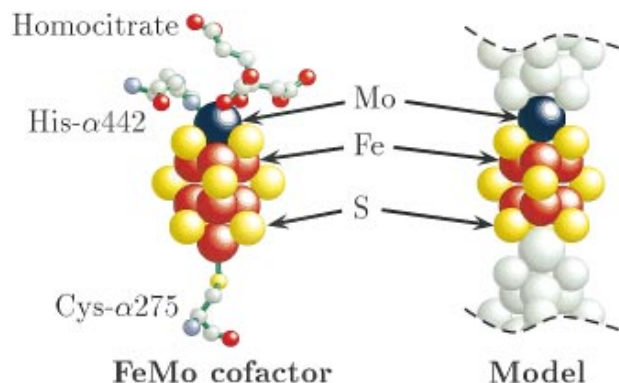


FIG. 1(color). The FeMoco with ligands (to the left) and the minimum energy structure of the one-dimensional model ( $\text{MoFe}_6\text{S}_9$ )<sub>n</sub> complex (to the right). Ligands are illustrated by balls and sticks while the FeMoco and model are illustrated by space-filling spheres. For the continuing model only one unit cell is colored. Color key: Fe: brown; Mo: dark blue; S: yellow; C: gray; O: red; and N: light blue.

total spin density of zero—all the Fe-Fe interactions are antiferromagnetic, consistent with experiment [11].

The model is best suited to study the chemistry associated with the six central Fe atoms, since all their nearest and next nearest neighbors are identical to those of the true FeMoco. The Mo atom, on the other hand, has sufficiently different surroundings that its chemistry may be somewhat different. We therefore concentrate in the present study on adsorption and reactions associated with the central Fe atoms. This does not exclude that reactions associated with the Mo atoms can be important in connection with the FeMoco, but we note that Mo can be exchanged for V or Fe in the enzyme without loss of the ability to produce ammonia [1,12] suggesting that Mo may not be the active site.

TABLE I. Comparison of experimental and calculated bond lengths. The Fe-Fe' bond length is the distance between opposite atoms in the two iron triangles and the Fe-Fe bond length is the distance between atoms in the same iron triangle (Fig. 1). The experimental bond lengths are extracted from crystallographic data, and except for the Fe-Fe' bond length only the three Fe and six S atoms closest to Mo are taken into account in order to compare with the model (Fig. 1). Both the experimentally determined and the calculated structure has a range of bond lengths, and we indicate that by giving the minimum and maximum values. The crystallographic coordinates are taken from Brookhaven Protein Data Bank (ID code 3min), published in Ref. [3].

Bond	Bond lengths (Å)	
	Experiment	DFT calculation
Fe-Fe'	2.48–2.60	2.56–2.58
Fe-Fe	2.45–2.61	2.46–2.54
Fe-μS	2.06–2.20	2.10–2.13
Fe-S	2.10–2.23	2.15–2.18
Mo-S	2.16–2.34	2.48–2.52

The model cannot be expected to describe the FeMoco in detail. It is, for instance, known that small changes in the ligands or the exchange of Mo for V or Fe can change the selectivity (the ratio of  $\text{H}_2$  to  $\text{NH}_3$  formation) of the FeMoco significantly [1,12]. Combined with the limited accuracy of the DFT calculations, this means that we concentrate on establishing a possible reaction pathway and on the general energetics of the reactions rather than on quantitative details.

We now continue with a discussion of the adsorption and reaction properties of the model compound. In the present Letter we consider only the stability of intermediates, not reaction barriers separating them. First, consider the adsorption of  $\text{N}_2$  on the neutral  $\text{MoFe}_6\text{S}_9$  complex. We will later consider complexes where the oxidation number has been reduced by adding hydrogen. We tried several adsorption sites, and the only one which gave a bond which is stable relative to  $\text{N}_2$  far from the complex is the one shown in Fig. 2(b).  $\text{N}_2$  adsorption strongly distorts

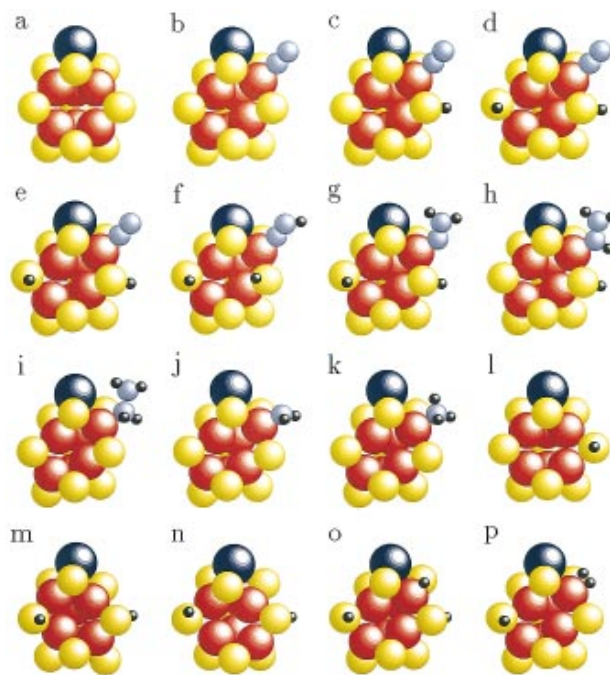


FIG. 2(color). Calculated structures of the lowest energy configuration of the  $\text{MoFe}_6\text{S}_9$  (a), with  $\text{N}_2$  adsorbed (b), with 1–3 H atoms [(c)–(e)], 4 H atoms [(f)–(i)], and with 5 and 6 H atoms [(j), (k)]. Also shown is the  $\text{N}_2$ -free complex with 1–4 H atoms [(l)–(o)] and with 2 H atoms and molecular  $\text{H}_2$  adsorbed (p). In case of the structures [(e), (f)] and [(o), (p)] the unseen H is bound to the hidden twofold coordinated S. All the structures are rotated  $60^\circ$  relative to Fig. 1 and only one unit cell is shown for each structure. All degrees of freedom of the system have been allowed to relax to minimize the energy of the system. In each case several different configurations have been considered, but we cannot exclude that configurations may exist that are not found by our energy minimization routine. The scenario presented is therefore a possible one, but not necessarily the only one. Same color key as in Fig. 1 and H atoms are black.

the complex, presumably in order to diminish the overlap between  $N_2$  and the S atoms. Changing the boundary conditions by varying  $c$  by 6% changes  $N_2$  adsorption energy by less than 30 meV indicating that the chemical reactivity does not depend on the boundary conditions. Ongoing molecular mechanics calculations also show that the structure in Fig. 2(b) is compatible with the rest of the protein [13].

We then added H atoms to the adsorbed  $N_2$  one by one. Addition of an H atom is a simple way of simultaneously adding an electron and a proton to the complex. Each time an H atom is added, several possible configurations were tried and the lowest energy structure was identified. We define the binding energy of the system by

$$\Delta E = E(X) - E(\text{MoFe}_6\text{S}_9) - n_H E(\text{H}) - n_{N_2} E(\text{N}_2), \quad (1)$$

where  $E$  is the calculated total energy of its argument, and  $n_H$  is the total number of adsorbed H atoms.  $X = \text{MoFe}_6\text{S}_9\text{H}_{n_H}$  when no  $N_2$  is added ( $n_{N_2} = 0$ ), and  $X = \text{MoFe}_6\text{S}_9\text{N}_2\text{H}_{n_H}$  when  $N_2$  is adsorbed ( $n_{N_2} = 1$ ).

Each of the hydrogenation steps for  $N_2$  on the  $\text{MoFe}_6\text{S}_9$  complex is strongly exothermic (Fig. 3). This is in contrast to the hydrogenation of gas phase  $N_2$ , where the addition of an H atom is thermoneutral or endothermic [14]. This shows an important role of the  $\text{MoFe}_6\text{S}_9$  complex in activating the  $N_2$  bond in analogy to other metal complexes [15]. Similar energetics has been obtained for the H

addition to  $N_2$  interacting with a  $\text{Fe}_2$  dimer sulfide [8] indicating that this is a general phenomena for iron sulfides.

In addition, we have added H atoms to the  $\text{MoFe}_6\text{S}_9$  part of the complex rather than to the adsorbed  $N_2$ . This does not change the overall energetics of subsequently adding H atoms to the  $N_2$  molecule (Fig. 3). By exploring all possible configurations with H atoms on the  $\text{MoFe}_6\text{S}_9$  complex and on the adsorbed  $N_2$  we construct the complete energy diagram, Fig. 3. For a given total number of H atoms, the lowest energy configuration gives the stablest intermediate, and by following these as the total number of H atoms is increased, the energetically preferred reaction path for the  $N_2$  hydrogenation can be deduced. After  $N_2$  has been adsorbed, the first three H atoms are stablest on the complex and not on the  $N_2$  molecule. But with the addition of the fourth, it becomes most favorable for all the H atoms to bind to the  $N_2$  molecule to form adsorbed hydrazine Fig. 2(i). This is then further hydrogenated to split off first one  $\text{NH}_3$  and then the next. Only the desorption of the last  $\text{NH}_3$  is endothermic. In principle we should include the possibility of adding another proton to form  $\text{NH}_4^+$ . This would make the final step more exothermic. We could also include solvent effects. This would again make desorption of ammonia more exothermic. The calculated structures of the reaction path suggested by the energy diagram are shown in Figs. 2(a)–2(k).

Using atomic H as the reference state in Fig. 3 is a matter of choice. Under “biological” turnover conditions, the H atom enters as a proton and an electron, which is transferred from the 4Fe-4S cluster in the Fe protein. The energy of each state with  $n_H$  H atoms in Fig. 3 should therefore be shifted by  $n_H[E(\text{H}) - E^{\text{bio}}(\text{H})]$ , where  $E^{\text{bio}}(\text{H})$  is the energy of the electron and proton added to the FeMoco during synthesis, and  $E(\text{H})$  is the atomic H energy used as reference in Eq. (1) and Fig. 3.  $E^{\text{bio}}(\text{H})$  will typically be higher than  $\frac{1}{2}E(\text{H}_2)$  by an energy  $\Delta E_{\text{H}}^{\text{bio}} = E^{\text{bio}}(\text{H}) - \frac{1}{2}E(\text{H}_2)$  which is given by the reduction energy of the  $[\text{4Fe-4S}]^{1+/2+}$  cluster at synthesis conditions and the energy funneled into the reaction during ATP hydrolysis.

In Fig. 4 we show the energy of the stablest intermediates from Fig. 3 using the energy  $E(\text{H}_2)$  per atom in  $\text{H}_2$  as the reference state. This corresponds to  $\Delta E_{\text{H}}^{\text{bio}} = 0$ . It can be seen that as long as the sum of the reduction energy and the energy from hydrolysis of ATP is moderately negative there is no state of the reaction path which is higher in energy than the reactants. This means that every state is thermodynamically accessible. Whether it is kinetically accessible depends on barriers which we do not consider here. We will, however, expect the proton transfer processes to be facile [16].

Figure 4 shows that with up to three H atoms on the cluster,  $N_2$  adsorption is reversible. With the  $N_2$  adsorption energy from the calculation, the  $N_2$  coverage will actually be quite small at room temperature and 1 bar of  $N_2$  in the gas phase. Transfer of the fourth H atom

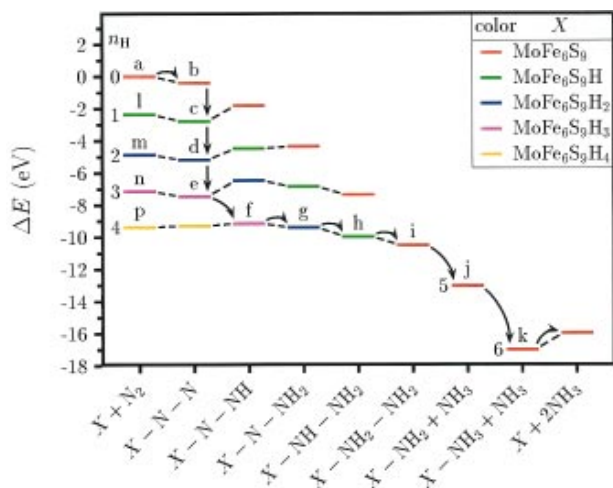


FIG. 3(color). The calculated binding energy  $\Delta E$  [Eq. (1)] of  $N_2$  and H to the  $\text{MoFe}_6\text{S}_9$  complex ( $X$ ). Along the horizontal axis we show whether  $N_2$  is adsorbed and how many H atoms are bound to the adsorbed  $N_2$ . Going down from one structure to the next in the vertical direction corresponds to the addition of hydrogen to the body of the complex. Energy bars for systems with the same total number of H atoms,  $n_H$  (on the  $N_2$  and on the body of the complex), are connected by dashed lines, and  $n_H$  is shown to the left of the leftmost bar. The arrows connect the stablest intermediates as  $N_2$  is adsorbed and H atoms are added one by one. The labels [(a)–(p)] refer to the corresponding structures in Fig. 2.

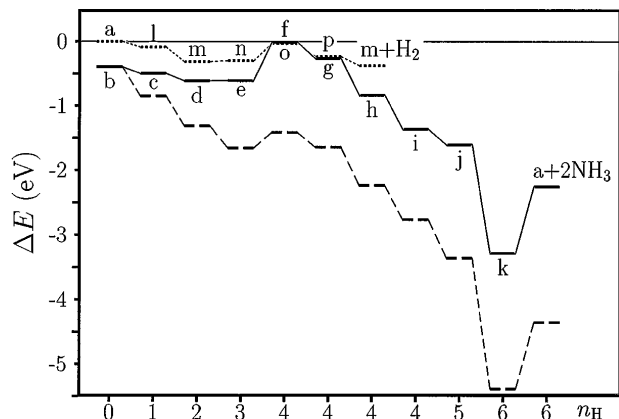


FIG. 4. Calculated binding energies for structures with  $n_H$  H atoms. Molecular hydrogen is used as the reference state for the dotted and solid bars. Dotted bars correspond to structures without  $N_2$  adsorbed, and solid bars to structures along the reaction path after  $N_2$  adsorption. The labels correspond to the structures shown in Fig. 2. Dashed bars are for the same structures as the solid bars but the H reference energy is given by  $\Delta E_H^{\text{bio}} = 0.35$  eV, cf. text. This value corresponds roughly to the measured reduction potential  $E^0 = -\Delta E_H^{\text{bio}}/e = -0.35$  V of the  $[4\text{Fe-4S}]^{1+/2+}$  cluster delivering the electrons [1]. (We concentrate here on the enthalpy part of the free energy.)

(electron and proton) will, however, transfer the whole system irreversibly to the much more stable state  $i$ , where hydrazine is formed. This is in good qualitative agreement with the kinetic model of Thorneley and Lowe [4].

Figure 4 also shows that  $H_2$  evolution is a competing reaction, and, in fact, may be as fast for the system considered here, since the first step with four H atoms is as stable without  $N_2$  adsorbed as with  $N_2$  adsorbed.

It is interesting to compare the proposed reaction on the model enzyme to the reaction taking place on Fe surfaces. Here it is known that the ammonia synthesis proceeds via  $N_2$  dissociation and subsequent hydrogenation of the adsorbed N atoms [17]. This is very different from the reaction studied in the present paper. We have found no tendency for  $N_2$  dissociation on the  $\text{MoFe}_6\text{S}_9$  complex. This, we suggest is the reason that the enzyme can function at room temperature, whereas the metallic Fe based catalysts have to function at about 700 K. The high temperature is primarily needed to keep the surface from being blocked by strongly bound atomic nitrogen [18]. The prize may be that molecular  $H_2$  is not quite energetic enough to make the reaction go, cf. Fig. 4.

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